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WC2A 1HZ (GB)(54) **Method of producing conversion coatings.**

(57) Corrosion resistant conversion coatings can be deposited on a metal, especially, zinc, tin, cadmium, iron, steel, magnesium, copper, nickel, silver or aluminium or their alloys, substrate by contacting the substrate with an aqueous solution containing Fe^{II}, Fe^{III}, Ni^{II} or especially Cr^{III} ions and an oxidizing agent. The solution is either dilute, less than 0.1 M, in respect of the ions and/or contains a weak complexing agent for the ions. Especially good corrosion resistance notably on Zn e.g. galvanized steel, substrates is obtained by including boric acid in the solution. The coatings are preferably baked to age them and may subsequently be lacquered, painted or laminated to plastics materials.

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METHOD OF PRODUCINGCONVERSION COATINGS

The present invention relates to the deposition of coatings on metal substrates and particularly to a method of depositing non-metallic conversion coatings containing hydrated metal oxides.

5 Chromium containing conversion coatings have been deposited under acid conditions from a Cr^{VI} solution containing sulphuric or nitric acids. Coatings deposited from solutions containing sulphuric acid are yellow-gold and those deposited from solutions containing nitric acid
10 tend to be slightly blue. These coatings contain Cr^{VI} and are also known as "chromate" coatings.

We have previously shown in British Patent Specification No. 1531056 and West German Offenlegungsschrift No. P 28 22 463 that it is possible to
15 electrodeposit highly satisfactory non-metallic coatings containing hydrated trivalent chromium oxides from a Cr^{III} electrolyte.

To our surprise, we have now discovered that non-metallic conversion coatings containing Cr^{III} , Fe^{II} ,
20 Fe^{III} or Ni^{II} can be obtained by a non-electrolytic method from a solution containing the corresponding metal ions.

The present invention provides a method of

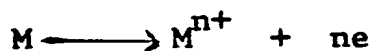
depositing a coating on a metal substrate which method comprises contacting a metal substrate to be coated with an aqueous solution comprising metal ions which are one or more of Cr^{III} , Fe^{II} , Fe^{III} or Ni^{II} ions in a concentration of up to 0.1 molar and an oxidizing agent to depolarize the reaction taking place at the surface of the substrate to be coated, whereby a coating is deposited on the surface of the substrate.

In another aspect, the present invention provides a method of depositing a coating on a metal substrate which method comprises contacting a metal substrate to be coated with an aqueous solution comprising metal ions which are one or more of Cr^{III} , Fe^{II} , Fe^{III} or Ni^{II} ions, a weak complexing agent for the metal ions and an oxidizing agent to depolarize the surface of the substrate to be coated, whereby a coating is deposited on the surface of the substrate.

The present invention particularly includes a method of depositing a Cr^{III} -containing coating on a metal substrate which method comprises contacting a metal substrate to be coated with an aqueous solution comprising Cr^{III} ions in a concentration of up to 0.1 molar and an oxidizing agent to depolarize the reaction taking place at the surface of the substrate to be coated. More particularly, the present invention includes a method of depositing a Cr^{III} -containing coating on a metal substrate comprising contacting the metal substrate with an aqueous solution comprising Cr^{III} ions, a weak complexing agent for Cr^{III} ions and an oxidizing agent to depolarize the surface of the substrate to be

coated, whereby a coating is deposited on the surface of the substrate.

The theoretical basis for the method of the present invention is different from that for the electrolytic method of chromite deposition described in British Patent Specification No. 1531056 and West German Offenlegungsschrift No. P 28 22 463. Thus, in the electrolytic method, the substrate to be coated is made to be the cathode (i.e. it is negatively charged) and, in the immediate vicinity of the cathode, various species present in the electrolyte react causing an increase in pH adjacent to the cathode. The rise in pH at the cathode causes the precipitation of chromite in the cathode film which leads to deposition of the chromite on the surface of the cathode. Contrary to this, in the method of the present invention the substrate behaves anodically where, at the surface of the substrate, the reaction



occurs, wherein M is the metal of the substrate, and $n+$ is the oxidation state of the M ion which passes into the aqueous solution in contact with the substrate. This oxidation reaction however liberates electrons which polarize the substrate. The aqueous solution comprises the metal ions and an oxidizing agent, and the latter acts to depolarize the reaction occurring at the surface of the substrate which causes an increase in the pH of the aqueous solution adjacent to the substrate, thus leading to the precipitation and deposition onto the substrate of a conversion coating.

In the case where no weak complexing agent is present in the aqueous solution, the practical minimum concentration of the metal ions used in the present invention will generally be 0.002 molar (about 0.1 gl^{-1} as the metal ion). Below this concentration, the reaction is too slow to be practical. Furthermore, as the concentration of the metal ions decreases below 0.002 molar, the solution becomes increasingly unstable. For instance, in the case of Cr^{III} -containing solutions, there is a serious risk of spontaneous precipitation of chromium-containing species out of the bulk solution as the Cr^{III} concentration falls below this value. The maximum concentration of the metal ions is 0.1 molar (about 5 gl^{-1} as the metal ion). Above this concentration, the coatings tend to be powdery and non-adherent. Typically, the method will be carried out using a solution having a concentration of the metal ions of from 0.03 to 0.08 molar (1.5 to 4 gl^{-1} as the metal ion) and preferably of from 0.04 to 0.06 molar (2 to 3 gl^{-1} as the metal ion) although the optimum concentration will depend on the particular operating conditions employed.

Much higher concentrations of the metal ions can be used in the aspect of the present invention where the solution contains a weak complexing agent for the metal ions; in such a case the concentration of the metal ions will generally be within the range of from 0.002 to 0.8 molar (0.1 to 40 gl^{-1} as the metal ion). At concentrations below 0.002 molar, the reaction is slow as in the case where no weak complexing agent is

used. At concentrations of the metal ions above 0.8 molar, the reaction at the surface of the substrate becomes so rapid that it tends to be non-selective giving rise to non-uniform coatings. However, there is no
5 advantage in using high concentrations of the metal ions since satisfactory coatings are obtained using lower concentrations. Furthermore higher capital costs and losses, such as dragout losses, are associated with the use of high concentrations of the metal ions.
10 Typically, when a weak complexing agent is used, the metal ion concentration is within the range of from 0.01 to 0.4 molar (0.5 to 20 gl^{-1} as the metal ion) and preferably from 0.04 to 0.1 molar (2 to 5 gl^{-1} as the metal ion) although the optimum concentration will
15 depend on the particular operating conditions.

By the term "weak complexing agent" we mean a complexing agent which forms a coordination complex with Cr^{III} , Fe^{II} , Fe^{III} or Ni^{II} sufficiently strong to maintain a salt in aqueous solution at a concentration
20 of 0.1 molar with the metal ion to weak complexing agent molar ratio of 2:1 at a pH of 6.0 but not at a pH of 9.0.

Within the definition the particular nature of the weak complexing agent is not especially critical.
25 Materials suitable for use as the weak complexing agent include hypophosphite ions (for Cr^{III} ions only), acetate ions, formate ions, citrate ions, glycine and glycollate ions, with hypophosphite ions (for Cr^{III} ions only), acetate ions and formate ions being preferred.
30 Although glycine, glycollate ions and citrate ions are

suitable, they are not preferred since they tend to complex with metal ions more strongly than is normally desired. When used, the weak complexing agent will generally be present such that the molar ratio of weak
5 complexing agent to the metal ions will be in the range of from 1:10 to 10:1, preferably from 0.3:1 to 2:1 optimally from 0.5:1 to 2:1.

The oxidizing agent is used in the present invention to depolarize the reaction at the surface of
10 the substrate. In the absence of an oxidizing agent, the low acidity of the solution causes the metal dissolution reaction, which results in protective film deposition, to be choked preventing the formation of coherent protective films. The use of the oxidizing
15 agent provides an alternative reaction path that does not require the presence of high concentrations of hydrogen ions to promote the dissolution and deposition reactions. The mode of action of the oxidizing agent causes a rise in the pH of the film of the solution
20 adjacent to the surface of the metal substrate which causes precipitation of hydrated metal oxides onto the substrate surface forming a coherent conversion coating. In order to depolarize the surface of the substrate, the redox potential of the oxidizing agent used must
25 be more positive than that of M/M^{n+} , i.e. the oxidizing agent must be able to oxidize M to M^{n+} , where M is the metal of the substrate surface and $n+$ is the oxidation state of the M ion obtained from the surface of the substrate. Furthermore, to be useful in the present
30 invention, the oxidizing agent should be stable to acid

and should be oxidizing under alkaline conditions.

Furthermore, the oxidizing agent should not attack the weak complexing agent, if present in the solution.

Suitable oxidizing agents include H_2O_2 , inorganic

5 peroxy anions which dissociate in aqueous solution to furnish hydrogen peroxide, and nitrate ions. Examples of peroxy anions include persulphates and perborates.

Examples of sources of nitrate ions include sodium nitrate and potassium nitrate. Preferably, the

10 oxidizing agent is hydrogen peroxide or sodium nitrate. Generally, the oxidizing agent is present in the solution in an amount of from 0.25 to 20 gl^{-1} since at concentrations of less than about 0.25 gl^{-1} the reaction is rather slow and at concentrations above 20 gl^{-1}

15 the reaction tends to become so rapid that the metal substrate dissolves quickly and the deposition of the chromite is not uniform. Typically the concentration of the oxidizing agent will be from 2 to 12 gl^{-1} , and most preferably from 5 to 8 gl^{-1} although the optimum

20 concentration will depend on the identity of the substrate and the metal ion used and the reaction conditions such as pH, temperature and the concentration of the metal ions. When a peroxide is used, it may be preferred to add one or more further materials to

25 stabilize the peroxy anion. Such materials are generally known in the art and include e.g. acetate ions. A stabilizer, when used however, must satisfy the criterion that it does not interfere with the other components in the solution.

Another oxidizing agent suitable for use in the present invention is the ferricyanide ion although this should not be used in the presence of metal ions which form insoluble complexes with ferricyanide ions. For this reason ferricyanide ions are not suitable for use in the presence of Fe^{II} , Fe^{III} and Ni^{II} ions. Ferricyanide, however, does have the advantage of being regenerable. In the oxidation reaction, ferricyanide is reduced to ferrocyanide. This ferrocyanide can be subsequently oxidized by adding, to the solution, a suitable oxidizing agent, such as hydrogen peroxide, to regenerate the ferricyanide. When used, the ferricyanide ion is generally present in the solution at a concentration of from 1 to 30 gl^{-1} . It may be conveniently be added as an alkali metal or the ammonium salt.

The source of the metal ions (Cr^{III} , Fe^{II} , Fe^{III}

and Ni^{II}) used in the present invention is not critical, provided that the anion in the salt used does not interfere with the reaction. Suitable salts include chromic sulphate, chromic chloride, ferrous ammonium sulphate and nickel chloride.

The presence of chloride ion in the solution has a beneficial effect, giving a more uniform conversion coating, and chloride ions, e.g. from NaCl , may be added to the solution, if desired. Generally, the concentration of chloride ions should be within the range of from 0.2 molar up to the saturation point of the chloride salt used, but not usually more than about 0.3 molar (10 g l^{-1} as Cl^-).

Conversion coatings obtained by the method of the invention may also contain other ions in addition to the one or more Cr^{III} , Fe^{II} , Fe^{III} and Ni^{II} ions, already present. Of course, these additional ions should not have adverse effects on the conversion coatings or interfere with the other components in the system. Because of this, Cr^{VI} , Ni^{III} and high oxidation state Mn ions should be excluded from the solutions used to carry out the method of the present invention. The solutions may, however, contain other ions which do not interfere with the deposition of the conversion coatings but which may actually alter or enhance the properties of the resulting conversion coatings, such ions include one or more of Mg, Al, Zn, Mn^{II} , Ti^{III} and Ti^{IV} ions which may be present in the solution at a concentration of 0.1 to 5.0 g l^{-1} (as the particular ion) and preferably 1 to 3 g l^{-1} . The resulting conversion coatings

comprise a mixture of hydrated oxides.

As far as the present invention is concerned, the term hydrated metal oxides is used to mean one or more oxides, hydroxides and hydrous oxides of the particular metal concerned.

Typical substrates which can be coated according to the invention include zinc (including zinc-galvanized tin (including tin plated steel), steel),/cadmium, iron, steel, in particular stainless steel, magnesium, copper, nickel and alloys of these metals. The method of the present invention may also be used to deposit a protective coating on aluminium. In referring to aluminium we include alloys of aluminium. Aluminium is generally resistant to corrosion because a thin but continuous film of oxide naturally forms on its surface. Aluminium is finding increasingly wider applications in which the surface of the metal is to be subsequently painted, lacquered or laminated to plastics. In such applications it has been found that the oxide film on the aluminium surface generally does not allow paint or lacquer to adhere strongly. Contrary to this, conversion coatings and in particular chromite coatings, produced by the method of the present invention, enhance the adhesion of paint or lacquer films. Furthermore, coating aluminium with a conversion coating is a generally quicker and cheaper process than the usual anodizing process. In order to coat aluminium with a hydrated metal oxide conversion coating it is necessary to remove the natural oxide film from the aluminium surface before the hydrated metal oxides can be deposited. The method of the present invention is

applicable to depositing a hydrated metal oxide conversion coating on an aluminium surface wherein the reaction solution also contains a material for dissolving away the natural aluminium oxide film. Such materials should not interfere with other materials in the solution. A preferred material is fluoride ion which acts on the aluminium oxide film to give water-soluble fluoroaluminate. If fluoride ions are not already present in the solution, a convenient source of F^- ions is provided by adding to the solution a fluoride salt such as sodium fluoride (or a material which furnishes fluoride ions in solution, such as fluoroborates and fluorosilicates). Generally, the concentration of fluoride in the solution will be in the range of from 1 to 20 gl^{-1} , optionally from 3 to 8 gl^{-1} (expressed as NaF) when added as a simple salt and from 3 to 15 gl^{-1} (as fluorosilicate) when added as a complex salt.

An alternative method of removing any aluminium oxide film from the surface of an aluminium or aluminium alloy substrate is to contact, preferably by immersion, the surface to be coated in a pretreatment bath prior to contacting the surface with the coating solution. This can be achieved conveniently by immersing the aluminium substrate in a pretreatment bath containing the material, preferably fluoride ions, for dissolving the alumina film and, then transferring the pretreated substrate, preferably without rinsing, to the coating solution. Of course, it may be desired to pretreat an aluminium surface some time before it is contacted with the coating solution and, in such a case, care must be taken to prevent the "clean" aluminium surface from re-oxidizing. Techniques for doing this are generally

well known, such as storage under N_2 .

The solution during the operation of the invention will normally be at ambient temperature, since satisfactory coatings are obtained at this temperature. However, higher
5 solution temperatures may be employed, if desired. In the absence of a weak complexing agent for metal ions, the temperature should, in general, not be above about $50^{\circ}C$ since above this temperature the reaction may become rapid and deposition non-uniform. When the solution contains a
10 weak complexing agent, slightly higher temperatures, such as up to about $80^{\circ}C$, can be tolerated. However, at these higher temperatures there is an increased risk of catastrophic reaction leading to increased dissolution of metal substrate

and deposition of non-uniform, poor quality films. However, when a weak complexing agent is present, typically the temperature will not be allowed to rise above 60°C.

- 5 The pH of the solution is moderately acid in the range of from 1 to 7. The choice of pH in any particular case will depend on the metal in solution and, to a minor extent, the nature of the substrate. Typical and optimum pH ranges are set out in the tables A and
- 10 B below, for solutions not containing and containing a weak complexing agent.

A. Solutions not containing a Weak Complexant

15

20

| <u>Ion in Solution</u> | pH Range | |
|------------------------|-----------|-----------|
| | Typical | Optimum |
| Cr III | 1.0 - 3.0 | 2.0 - 3.0 |
| Fe II | 2.0 - 6.0 | 2.5 - 4.5 |
| Fe III | 1.0 - 3.0 | 1.5 - 2.5 |
| Ni II | 3.0 - 6.5 | 3.5 - 6.0 |

B. Solution containing a Weak Complexant

25

30

| <u>Ion in Solution</u> | pH Range | |
|------------------------|-----------|-----------|
| | Typical | Optimum |
| Cr III | 2.0 - 5.5 | 2.5 - 4.5 |
| Fe II | 2.0 - 7.0 | 2.5 - 4.5 |
| Fe III | 1.5 - 5.5 | 2.0 - 5.0 |
| Ni II | 3.5 - 7.0 | 4.0 - 6.5 |

It has surprisingly been found that conversion coatings with unexpectedly improved corrosion resistance can be deposited from solutions which contain boric acid in addition to the above-described components. For
5 certain applications, for instance where the coated substrate is intended for use in a corrosive environment eg marine applications, the improvement in corrosion resistance afforded by the use of boric acid may be of great importance. Since coatings produced from boric
10 acid-containing solutions tend to be opaque, or at least clouded, the use of boric acid is not suitable where transparent and colourless coatings are desired, for instance on ornamental silverware.

The presence of boric acid in the coating solution
15 increases the rate of deposition of the coating thereby enabling the formation of thicker coatings in a given treatment time. Although, the mechanism by which boric acid achieves this is not fully understood, a major contribution to this effect is made by the power
20 of the boric acid present in solution to act as a pH buffer. In controlling the pH drift at the substrate surface the boric acid aids the formation and flocculation of the metal oxide/hydroxide precipitate in this region. The buffering power of boric acid in aqueous solutions is
25 at a maximum in the range of pH 4 to 6 and it is in this pH range that the best results might be expected. Thus it can be seen that the typical and optimum pH ranges listed in Tables A and B above do not, in most cases, apply to solutions containing boric acid.

The increase in corrosion resistance of conversion coatings deposited from boric acid-containing solutions is thought to be partly due to the fact that certain borate-containing species are occluded into the coatings during deposition. In a solution containing aluminium or titanium ions, hard, resistant aluminoborates or titanoborates may be formed and occluded into the conversion coating deposited. The occlusion of these borate-containing species are of considerable importance since when, during use, the conversion coating is in contact with a corrosive aqueous solution the borates, by their buffering action, tend to "choke" any galvanic reaction which would normally lead to corrosion occurring at the surface of a coated substrate.

When used, in the present invention the boric acid will usually be added to the solution to give a boric acid concentration in the range of from 1 to 40 gl^{-1} , preferably from 5 to 25 gl^{-1} .

When it is desired to coat aluminium or aluminium-alloy surfaces using boric acid-containing treatment solutions, care must be taken about the use of the free fluoride ions. As described above, fluoride ions are especially useful for dissolving away oxide films formed on aluminium surfaces. Unfortunately, free fluoride ions react with the boric acid, and the borate ions derived therefrom, to give various fluoroborate species and, ultimately, boron tetrafluoride ions. The problem can, to some extent, be avoided by adding boric acid and sufficient fluoroborate to ensure adequate concentration of fluoride ions. Alternatively, instead of adding free fluoride ions directly to the boric acid-containing

solution, one can add a material such as a fluorosilicate or a fluoroborate which releases fluoride ions in a slow and controlled manner. Preferably, the risk of a "mopping-up" reaction between fluoride ion and boric acid is removed by pretreating an aluminium surface to be coated in a fluoride-containing bath to dissolve away the oxide film and then transferring the treated aluminium surface to the coating solution. Usually the pretreated aluminium surface will be transferred immediately to the coating solution preferably without rinsing.

Using the conditions described previously, contact of the substrate with the reaction solution for a period of only a few seconds will be sufficient to give a film on the substrate. In general, the period of time of contact will depend on the thickness of the layer desired which, in turn, will depend on how the coated substrate will be used. Typically, the period of time for which the substrate is in contact with the reaction solution will be from 5 seconds to 20 minutes, and more usually from 30 seconds to 5 minutes.

The method of the present invention can be easily carried out either on a batch wise or a continuous basis. Many existing commercial practices for depositing conversion coatings have been designed to maximise the throughput of work and the present invention is particularly suited to a "no-rinse" system, in which the substrate to be coated, for instance metal tape or sheet, is immersed in the treatment bath for a period such as 3 to 15 seconds. After the re-emergence of the

substrate from the treatment bath, the treatment solution retained on the surface of the substrate would not be washed off but would be allowed to continue the reaction with the metal surface until it dried. By this method conversion coating thicknesses appropriate to longer immersion times can be produced.

It is within the scope of the present invention that a substrate to be coated is not immersed in the treatment bath but is, instead, sprayed with the coating solution which then reacts with the metal substrate surface.

Freshly deposited films are soft and can be removed from the substrate by mild abrasion. The films can, however, be hardened and made more resistant to mechanical abrasion by air drying, usually for not less than 24 hours. Preferably, however, the coated substrates are dried in an oven at temperatures of greater than about 40°C for not less than half an hour, preferably 100° - 110°C for about one hour. It is important, however, that the drying conditions used should not be severe enough to disrupt the coating.

An alternative method of drying freshly deposited coatings is to pass the coated substrate through a dewatering fluid. The use of dewatering fluids is generally well known. The solutions of the present invention are relatively non-reactive to the organic compounds present in dewatering fluids, thus enabling a dewatering step to be used as an alternative to rinsing after immersion in the conversion coating solutions. The advantage provided by the use of dewatering fluids instead of rinsing is that no drag out of conversion coating solution results and effluent treatment problems are removed or substantially

reduced. Dewatering fluids, additionally containing corrosion inhibitors or waxes, can be used to improve the corrosion resistance of the coating since on evaporation of the dewatering fluid the corrosion inhibitor or wax remains on the surface of the specimen. Dewatering fluids generally comprise a water-immiscible solvent, and preferably also a surfactant and a carrier solvent for the surfactant. The surfactant acts to displace water from the surface of the coated metal substrate. For this reason the surfactant will have a low solubility in water, for example surfactants having long chain aliphatic groups. The solvent is typically "white spirit", kerosene or a light mineral oil. Corrosion inhibitors for zinc can be 2,5 dimercapto-thiadiazole, dithio-oxamide and several other compounds well known in the art.

The typical short time of contact of the substrate with the reaction solution allows the method of the present invention to be carried out on a continuous, as well as a batch-wise, basis. For instance, a continuous metal tape or strip may be drawn through a vat containing a reaction solution according to the present invention at a speed such that the tape or strip, on leaving the vat, has the desired thickness of film.

The conditions employed in the method of the present invention are such that, in general, conversion

coatings having a thickness of from 0.01 to 5 μm may be obtained. Of course, the thickness of the coating will be determined by its intended purpose and the intended use of the coated substrate. Thus, for most industrial applications where the conversion coating is intended to protect the surface of the substrate from corrosion, generally a thickness of from 1 to 5 μm will be desired. It may be desirable to provide decorative silver articles with a conversion coating which will protect the silver surface from corrosion during storage of the articles. Silver articles may be treated according to the present invention, preferably using a Cr^{III} - containing solution together with peroxide as oxidizing agent to provide them with protective chromite coatings of a suitable thickness which is generally about 0.05 μm . If a conversion coating is to be deposited as a "key" layer onto a substrate in order to enhance the adhesion of subsequent paint or lacquer films, a conversion coating thickness of from 0.1 to 1.0 μm is acceptable for most applications.

Usually, it will be preferred to make up a concentrate of the reaction solution containing all of the components except the oxidizing agent. Such a concentrate can be stored and, when required for use, can be diluted as desired followed by the addition of the oxidizing agent. This practice is particularly preferred when peroxides, especially hydrogen peroxide are used as the oxidizing agent since peroxides tend

to be unstable when stored in the presence of heavy metal ions such as Cr^{III} ions. Typically, a Cr^{III} containing concentrate would contain Cr^{III} in a concentration of from 40 to 50 gl^{-1} as Cr^{III} .

5 The conversion coatings obtained by the method of the invention may serve as primer coatings for subsequent coatings of paint or lacquer. In particular, a chromite film secures enhanced adhesion of the paint or lacquer coating. Moreover, the conversion coating provides
10 additional protection against corrosion by suppressing under-film corrosion of substrate metal. The coatings may also be used to key layers of plastics materials to the metal substrates to produce laminates.

 The invention will be illustrated by the following
15 Examples. Chrometan is a commercially available basic chromic sulphate having the approximate stoichiometric formula $3\text{Na}_2\text{SO}_4 \cdot 2\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ when $n < 1$ and which yields 1 gl^{-1} chromic ion per 6.25 gl^{-1} . ASTM
test No. B - 117 was used in the neutral salt spray
20 test.

Example 1

A steel panel was electroplated with zinc from a bright plating solution to a thickness of 10 μm . After plating, the zinc plate was brightened by immersion in
25 0.1% nitric acid and then dried at 60°C for 1 hour. The panel was exposed to 5% neutral salt spray. Deterioration was evident after 1 hour and massive zinc corrosion products (white rust) were evident after 4 hours.

A second steel panel, electroplated and brightened in the same way and then immersed in a solution containing 25 gl^{-1} chrometan for two minutes at a temperature of 25°C and pH 3.0. The panel was rinsed and dried at 60°C for 1 hour and then salt spray tested as before. Rapid corrosive attack occurred.

A third steel panel was processed in the same way except that after plating and brightening, it was immersed for two minutes in a solution containing 25 gl^{-1} chrometan and 12 gl^{-1} sodium hypophosphite at a temperature of 25°C and pH 3.0. On salt spray testing, rapid corrosion of the zinc occurred.

A fourth panel was processed in the same way except that after plating and brightening, the panel was immersed for two minutes in a solution containing 25 gl^{-1} chrometan, 12 gl^{-1} sodium hypophosphite, 8 gl^{-1} sodium nitrate pH = 3.0, temp = 25°C . No corrosion was evident after 24 hours of salt spray testing.

Example 2

A solution containing 240 gl^{-1} chrometan and 120 gl^{-1} sodium hypophosphite was prepared. A passivating solution was prepared by diluting 1 part of this concentrate with 9 parts of water and adding 8 gl^{-1} sodium nitrate.

Steel panels, zinc electroplated and brightened as in Example 1, were immersed in this solution for times varying from 10 seconds to 20 minutes, at temperatures in the range of 15°C to 75°C and pH values in the range 1.0 to 4.5. After drying the passivated panels were salt spray tested. All panels survived

4 hours testing but panels passivated at pH values below 1.7, temperatures above 55°C and immersion times less than 20 seconds began to corrode after 24 hours of testing. All other panels survived at least 30 hours of testing.

Example 3

A passivating solution was prepared in the same way as in Example 2, except that the sodium nitrate was omitted and 12 ml l⁻¹ of hydrogen peroxide (30% w/v) added. A steel panel was zinc plated and brightened as in Example 1 and then immersed for 2 minutes in the passivating solution operated at pH = 3.0 and temperature of 25°C. There was no corrosion of the zinc after 24 hours of salt spray testing.

Example 4

A passivating solution was prepared by dissolving 12 gl⁻¹ chrometan (= 2.0 gl⁻¹ chromic ion) in water and adding 8 gl⁻¹ sodium nitrate. A steel panel, zinc plated and brightened as in Example 1, was immersed in the passivating solution for 4 minutes at a temperature of 25°C and a pH 3.0. No corrosion was evident after 24 hours of salt spray testing.

Example 5

A steel panel was plated with 10 µm of zinc from a dull acid zinc plating solution (a solution typically used for electrogalvanizing). The zinc plate was passivated by immersion for 2 minutes in a solution containing 24 gl⁻¹ chrometan, 12 gl⁻¹ sodium hypophosphite 6 gl⁻¹ sodium nitrate at a temperature of 25°C and pH 3.0. No corrosion was evident after 24 hours of salt spray testing.

Example 6

5 A steel panel zinc plated and brightened as in Example 1 was passivated by immersion for 2 minutes in a solution containing 24 gl^{-1} chrometan, 10 gl^{-1} sodium formate and 8 gl^{-1} sodium nitrate; the solution was maintained at a pH = 3.0 and temperature of 25°C. No corrosion was evident after 24 hours of salt spray testing.

Example 7

10 The experiment of Example 6 was repeated except that the passivating solution contained 10 gl^{-1} glycine instead of sodium formate. No corrosion was evident after 4 hours of salt spray testing, but the panel was unacceptably corroded after 24 hours of salt spray
15 testing.

Example 8

A steel panel was cadmium plated and then passivated by immersion for 2 minutes in a passivating solution containing 24 gl^{-1} chrometan, 12 gl^{-1} sodium hypophosphite, 8 gl^{-1} sodium nitrate at a temperature
20 of 25°C and pH 3.0. This panel did not show any corrosion after 24 hours of salt spray testing. A similar unpassivated cadmium plated steel panel was corroded after only 8 hours of salt spray testing.

Example 9

25 A brass panel was copper plated, rinsed and then passivated by immersion for 2 minutes in a solution containing 24 gl^{-1} chrometan, 12 gl^{-1} sodium hypophosphite and 5 ml l^{-1} hydrogen peroxide (30% w/v) at a temperature
30 of 25°C and pH 3.0. After drying, the panel was immersed in a polysulphide solution; no blackening of the copper was evident after 30 seconds immersion.

A similar unpassivated copper plated brass panel, blackened immediately on immersion in the polysulphide solution.

Example 10

5 Aluminium panels were degreased and immersed for 30 secs. in a solution containing 24 gl^{-1} chrometan, 8 gl^{-1} sodium nitrate and 5 gl^{-1} sodium fluoride at pH 3.5, and a temperature of 30°C . The panels were rinsed and air dried at 100°C for one hour. These
10 samples were subjected to a 5% neutral salt spray test alongside panels of the same aluminium alloy that had received no immersion treatment. After 96 hours testing the untreated samples showed extensive corrosion. The treated samples were in the same condition as at the
15 commencement of the test. The passivating film was iridescent.

Example 11

Aluminium panels were degreased and immersed for 30 secs. in a solution of the composition stated in
20 Example 10 but containing additionally 12 gl^{-1} sodium hypophosphite. The immersion conditions were as in Example 10. An iridescent passivating film was deposited that provided excellent corrosion protection to the aluminium alloy in salt spray testing. No
25 deterioration in appearance was evident after 200 hours salt spray testing.

Example 12

Degreased aluminium panels were protected by immersion in a solution containing 1 gl^{-1} chromium III
30 cation, 5 gl^{-1} sodium hypophosphite and 5 gl^{-1} sodium nitrate and 5 gl^{-1} sodium fluoride. The pH of the solution was a) 4 b) 3 c) 2 at temperature 30°C .

All samples were rinsed and dried in air at 100°C. Excellent corrosion resistance was conferred to all panels when exposed to neutral salt spray.

Example 13

5 A solution containing 4 gl^{-1} of nickel (as nickel chloride) and 8 gl^{-1} sodium nitrate was prepared. The pH was adjusted to 5.5 and the temperature maintained at 50°C. A steel panel, zinc plated and brightened as in Example 1 was immersed in this solution for 10
10 minutes. No corrosion was evident after 24 hours of salt spray testing.

Example 14

The experiment of Example 13 was repeated using a solution containing 4 gl^{-1} iron (as ferrous ammonium
15 sulphate) and 8 gl^{-1} sodium nitrate, pH = 3.0, temperature = 25°C. The panel was immersed in this solution for 2 minutes. No corrosion was evident after 2 hours of salt spray testing. Slight corrosion was evident after 4 hours testing and widespread corrosion after
20 24 hours testing.

Example 15

A solution was prepared containing 2 gl^{-1} of Cr^{III} (as chromic sulphate), 2 gl^{-1} of Al^{III} (as aluminium sulphate), 8 gl^{-1} NaNO_3 and 4 gl^{-1} hypophosphite (as
25 sodium hypophosphite). The solution was adjusted to pH 3.5 and maintained at a temperature of 25°C. A zinc plated steel panel was immersed in the solution for 2 minutes and dried. The panel exhibited a salt spray resistance of 100 hours when subjected to neutral
30 salt spray corrosion testing.

Example 16

A solution containing 24 gl^{-1} chrometan, 12 gl^{-1} sodium hypophosphite and 8 gl^{-1} sodium nitrate was prepared and the pH adjusted to 3.0. Zinc-plated steel panels were immersed in the solution at ambient temperature for 1 minute. The panels were rinsed and dried. A pale blue coating could be seen on the surface of the zinc. 10 gl^{-1} of boric acid was added to the solution and a second set of identical panels were treated in the same way. The appearance of the second set of panels was the same as the first set. The pH of the solution containing boric acid was raised by the addition of 10% NaOH solution until precipitation of chromic hydroxide could be detected, and the precipitate did not re-dissolve on standing. A third set of panels was treated in this solution. After rinsing and drying these panels were of a green colour.

The three sets of panels were corrosion tested in a salt-spray cabinet. Corrosion of the zinc on specimens in the first two sets was evident after 48 hours of salt-spray testing. Panels of the third set did not exhibit any zinc corrosion after 300 hours testing.

Example 17

The same experiments as in Example 16 were performed with the exception that the passivating solution did not contain sodium hypophosphite. The first two sets of panels exhibited zinc corrosion after 48 hours of salt-spray testing but the third set did not exhibit any corrosion after 200 hours of salt spray testing.

Example 18

A solution containing 18 gl^{-1} chrometan, 7.5 gl^{-1} sodium fluoride and 10 gl^{-1} sodium nitrate was prepared

and the pH of this solution adjusted to 2.5. Aluminium panels were degreased, etched, desmutted and rinsed and then immersed for 30 seconds in the conversion coating solution at 25°C. After rinsing and drying, the panels were subjected to salt-spray testing and survived more than 1,000 hours of test. A second set of panels was prepared as above and immersed for 2 seconds only in the conversion coating solution at 20°C. After rinsing and drying, the panels were subjected to salt-spray testing and survived only 100 hours of test. A third set of panels were identically processed except that, after immersion for two seconds in the conversion coating solution, the panels were dried without rinsing; these panels survived more than 1,000 hours of salt-spray test.

Example 19

A solution containing 24 gl^{-1} chrometan, 12 gl^{-1} sodium hypophosphite and 8 gl^{-1} sodium nitrate was prepared and the pH of the solution adjusted to 3.0. Zinc plated steel panels were immersed for 1 minute in this solution at 25°C. On removal, the panels were immersed, in Dewatering Fluid IL 968, ex. Esso Ltd., for 2 minutes. After this treatment, the conversion coating solution was completely removed from the surface of the specimens which were then filmed with the dewatering fluid.

Example 20

A solution containing 24 gl^{-1} chrometan, 12 gl^{-1} sodium hypophosphite and 10 gl^{-1} potassium ferricyanide was prepared; the pH of the solution was adjusted to 3.0 and the operating temperature was 25°C. Zinc plated

steel panels were immersed in the solution for 60 seconds and after rinsing and drying were subjected to salt-spray testing. The specimens survived 24 hours of salt-spray test. Similar panels, treated in the solution not
5 containing ferricyanide, were severely corroded after only four hours salt-spray testing.

Example 21

A steel panel was electroplated with 5 μ m tin, dried and immersed for 3 minutes in a conversion coating solution
10 containing

24 gl^{-1} chrometan
12 gl^{-1} sodium hypophosphite
6 ml l^{-1} 30% w/v aqueous H_2O_2
15 pH adjusted to 2.1, temperature 25°C.

After air drying the panel was subjected to neutral salt spray testing and no tin corrosion products were detected after 24 hours of testing. For comparison a
20 similar tin plated steel panel which was not conversion coated was salt spray tested and after 8 hours of testing the tin surface was severely discoloured with tin corrosion products.

Example 22

25 Four aluminium panels and four electrogalvanized steel panels (10 μ m Zn) were conventionally cleaned and pretreated for conversion coating. Two conversion coating solutions

were made up containing (respectively):

| | | | | |
|----|---------------------|-----------------|---------------------|----------------------|
| | 18 gl ⁻¹ | chrometan | 18 gl ⁻¹ | chrometan |
| | 4 gl ⁻¹ | sodium fluoride | 12 gl ⁻¹ | sodium hypophosphite |
| 5 | 7 gl ⁻¹ | sodium nitrate | 4 gl ⁻¹ | sodium fluoride |
| | | | 7 gl ⁻¹ | sodium nitrate |
| | pH adjusted to 2.5 | | pH adjusted to 2.5 | |
| 10 | temperature=25°C | | temperature = 25°C | |

Two of the aluminium and two of the galvanized steel panels were immersed in each of the solutions for 1 minute to conversion coat them. The eight panels were rinsed in water, air dried for 48 hours at ambient temperature and electrostatically powder painted. Each panel was scribed in a cross hatch pattern through the coating to the substrate metal. All the panels were subjected to neutral salt spray testing all surviving 500 hours and subsequently subjected to 300 hours of humidity testing (also according to ASTM test No. B-117). Examination of the panels showed that they all passed according to the standard because they showed no sign of underfilm corrosion or loss of paint adhesion.

CLAIMS:

1. A method of depositing a conversion coating on a metal substrate which method comprises contacting the metal substrate with an aqueous solution comprising metal ions which are one or more of Cr^{III} , Fe^{II} , Fe^{III} or Ni^{II} ions, a weak complexing agent for the metal ions and an oxidizing agent to depolarize the reaction taking place at the surface of the substrate to be coated, whereby a conversion coating is deposited on the substrate.
2. A method of depositing a conversion coating on a metal substrate which metal comprises contacting the metal substrate with an aqueous solution comprising metal ions which are one or more of Cr^{III} , Fe^{II} , Fe^{III} , or Ni^{II} ions, in a concentration not exceeding 0.1 molar and an oxidizing agent to depolarize the reaction taking place at the surface of the substrate to be coated, whereby a conversion coating is deposited on the surface of the substrate.
3. A method as claimed in either claim 1 or claim 2, wherein the solution includes one or more of Mg^{II} , Al^{III} , Zn^{II} , Mn^{II} , Ti^{III} or Ti^{IV} in addition to the said metal ions.
4. A method as claimed in claim 1 wherein the concentration of the said metal ions is from 0.002 to 0.8 molar.
5. A method as claimed in claim 2 wherein the concentration of the said metal ions is from 0.04 to 0.06 molar.
6. A method as claimed in any one of claims 1, 2, 4 and 5 wherein the metal ions consist of Cr^{III} ions.

7. A method as claimed in either claim 1 or claim 4, wherein the weak complexing agent is one or more of hypophosphite, acetate and formate ions.
8. A method as claimed in any one of claims 1, 4 and 7 wherein the molar concentration ratio of the weak complexing agent to the said metal ions is from 0.3:1 to 2:1.
9. A method as claimed in any one of claims 1 to 8 wherein the ^{oxidizing agent} is one or more of nitrate ions, hydrogen peroxide, peroxide ions and ferricyanide ions.
10. A method as claimed in claim 9 wherein the poison is nitrate ions at a concentration of from 2 to 12 gl^{-1} .
11. A method as claimed in any one of claims 1 to 10 wherein the substrate is zinc, ^{tin,} cadmium, iron, steel, magnesium, copper, nickel, silver or aluminium or their alloys.
12. A method as claimed in claim 11 wherein the substrate is aluminium or an aluminium alloy and wherein the substrate is treated to remove oxide film from the surface by contact with fluoride ions in aqueous solution either before or during deposition of the conversion coating.
13. A method as claimed in any one of claims 1 to 12 wherein the solution contains boric acid or borate ions at a concentration of from 1 to 40 gl^{-1} .
14. A method as claimed in any one of claims 1 to 13, wherein the substrate is in contact with the solution for a period of from 5 seconds to 20 minutes whereby a conversion coating having a thickness of from 0.01 to 5 μm is deposited thereon.
15. A method as claimed in any one of claims 1 to 14,

wherein the substrate is subsequently dried, optionally with prior rinsing, or dewatered.

16. A method as claimed in any one of claims 1 to 15 wherein the conversion coating on the substrate is subsequently aged or baked to render it more hard and resistant to mechanical abrasion.
17. A method as claimed in any one of claims 1 to 16 wherein the substrate is subsequently painted, lacquered or laminated to a layer of a plastics material.



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EUROPEAN SEARCH REPORT

0034040
Application number
EP 81 30 0467

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl.) |
|-------------------------------------|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| X | <u>US - A - 4 171 231</u> (C.V. BISHOP) * Claims 1,3,5,10; column 4, lines 15-20; column 6, line 61 - column 7, line 7 * | 1,2,4-7,9,11,14,15,17 | C 23 F 7/00 |
| | -- | | |
| | <u>US - A - 3 066 055</u> (G.H. PIMBLEY) * Claims 8-12; example 2, column 10 * | 1,2,5,6,9,11-15 | |
| | -- | | |
| | <u>GB - A - 394 211</u> (PYRENE COMPANY) * Claims 1,7 * | 2,10 | TECHNICAL FIELDS SEARCHED (Int. Cl.) |
| | -- | | |
| | <u>NL - A - 77 09404</u> (T.N.O.) * Example; page 5, lines 5-13 * | 2,3,6,9,11,14 | C 23 F 7/00 7/26 |
| | -- | | |
| A | <u>DE - C - 974 713</u> (METALLGESELLSCHAFT) | | |
| A | <u>US - A - 1 973 612</u> (M.H. CORBIN) | | |
| A | <u>US - A - 3 468 724</u> (E.R. REINHOLD) | | |
| | ---- | | |
| | | | CATEGORY OF CITED DOCUMENTS |
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| | | | &: member of the same patent family, corresponding document |
| X | The present search report has been drawn up for all claims | | |
| Place of search The Hague | | Date of completion of the search 27-04-1981 | Examiner TORFS |

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